Exactly Solvable Model of a Magnetic Impurity

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A slight modification of the "mixing" term in Anderson's model of a magnetic impurity produces an exactly solvable model. Results of some preliminary calculations are given, and upper and lower bounds on Anderson's model are obtained by means of the exact solutions.

Anderson's model of a magnetic impurity in a nonmagnetic host metal,[1] originally solved by him in a self-consistent approximation, has resisted exact solution to this day despite many frontal assaults.[2,3] The basic difficulty seems to be that the intrinsically nonlinear Coulomb repulsion term $Un_{d\uparrow}n_{d\downarrow}$ may not be treated as a small perturbation. On the contrary, in physically interesting cases it is desirable to consider arbitrarily large values of U. I have newly found that a somewhat modified model Hamiltonian can be manipulated in such a manner that this Coulomb term becomes linear and, regardless of magnitude, succumbs to conventional diagonalization techniques.

Like Anderson's, the new Hamiltonian has three parts: Bloch-state energies, a "mixing" term, and the Coulomb term:

$$\mathcal{H}=\sum_{km}\epsilon_{km}n_{km}+(\lambda/\sqrt{N})\sum_{km}V_k(c_{km}^*-c_{km})(c_{dm}^*+c_{dm})+U(n_{d\uparrow}-\tfrac{1}{2})(n_{d\downarrow}-\tfrac{1}{2})-\tfrac{1}{4}U, \tag{1}$$

expressed in terms of anticommuting fermion field operators c_α and occupation numbers $n_\alpha=c_\alpha^*c_\alpha$. It is an obvious modification of Anderson's Hamiltonian[1,2] (with $U=-2E_d$, and V_k assumed henceforth to be real), denoted by $\mathcal{H}_A$:

$$\mathcal{H}_A=\mathcal{H}-(\lambda/\sqrt{N})\sum_{km}V_k(c_{km}^*c_{dm}^*+\text{H.c.})\equiv\mathcal{H}+\mathcal{H}'. \tag{2}$$

Unlike the Coulomb term, the correction term $\mathcal{H}'$ may be viewed as multiplied by a small parameter λ even in the physically interesting regime. We shall subsequently show that the ground-state energy of $\mathcal{H}_A$, and the free energy at finite T, fall within narrowly prescribed upper and lower bounds which can be calculated using our $\mathcal{H}$.

The transformation of (1) to a linear form (quadratic rather than quartic in the field operators) proceeds via a sequence of three nonlinear steps. The operators $c_{k\downarrow}$ and $c_{k\downarrow}^*$ are not affected by any of these operations. In the first step, I, the operators of impurities c_{dm} and c_{dm}^* are replaced by pseudospin paulion operators, as are the Bloch-state operators $c_{k\uparrow}$ and $c_{k\uparrow}^*$. In the second step, II, the pseudospin operators of the impurities are rotated such that $S_{d\uparrow z}\rightarrow S_{d\downarrow y}$ and $S_{d\uparrow z}\rightarrow S_{d\uparrow x}$. Finally, III, the resultant paulions are replaced by new fermion operators, and $\mathcal{H}$ becomes a solvable quadratic form in the latter. More explicitly, the pseudospin operators are defined in terms of the c's as follows:

I. (i) All $c_{k\downarrow}$, $c_{k\downarrow}^*$ stay the same. (ii) Set

$$c_{d\downarrow}\equiv S_{d\downarrow -}\exp(i\pi\textstyle\sum n_{k\downarrow})\text{ and }c_{d\downarrow}^*\equiv\exp(i\pi\sum n_{k\downarrow})S_{d\downarrow +}.$$

(Sums are over all Bloch states $\vec{k}$ in the Brillouin zone.) (iii) Set

$$c_{d\uparrow}\equiv S_{d\uparrow -}\exp[i\pi(\textstyle\sum n_{k\downarrow}+n_{d\downarrow})]\text{ and }c_{d\uparrow}^*\equiv\exp[i\pi(\sum n_{k\downarrow}+n_{d\downarrow})]S_{d\uparrow +}.$$

Note:

$$n_{d\downarrow}\equiv c_{d\downarrow}^*c_{d\downarrow}=S_{d\downarrow z}+\tfrac{1}{2}\text{ and }n_{d\uparrow}=c_{d\uparrow}^*c_{d\uparrow}=S_{d\uparrow z}+\tfrac{1}{2}.$$

(iv) Set

$$c_{k\uparrow}\equiv a_{k\uparrow}\exp[i\pi(\textstyle\sum n_{k\downarrow}+n_{d\downarrow}+n_{d\uparrow})],$$

$$c_{k\uparrow}^*\equiv\exp[i\pi(\textstyle\sum n_{k\downarrow}+n_{d\downarrow}+n_{d\uparrow})]a_{k\uparrow}^*.$$

We note that the S operators *commute* with the a's and c's and that a's and c's also commute with one another but *anti*commute among themselves.

In terms of the new operators, we have

$$\sum_{km}\epsilon_{km}c_{km}{}^{*}c_{km}\rightarrow\sum_{k}\epsilon_{k\downarrow}c_{k\downarrow}{}^{*}c_{k\downarrow}+\sum_{k}\epsilon_{k\uparrow}a_{k\uparrow}{}^{*}a_{k\uparrow}, \tag{I.1}$$

and

$$U(n_{d\uparrow}-\tfrac{1}{2})(n_{d\downarrow}-\tfrac{1}{2})\rightarrow US_{d\uparrow z}S_{d\downarrow z}, \tag{I.2}$$

and lastly,

$$\sum_{km}V_{k}(c_{km}{}^{*}-c_{km})(c_{dm}{}^{*}+c_{dm})\rightarrow\sum_{k}[V_{k}c_{k\downarrow}{}^{*}\exp(i\pi\textstyle\sum n_{k\downarrow})+\text{H.c.}](S_{d\downarrow}{}^{+}+S_{d\downarrow}{}^{-})$$
$$-\sum_{k}(V_{k}a_{k\uparrow}{}^{*}-\text{H.c.})(S_{d\uparrow+}-S_{d\uparrow-}). \tag{I.3}$$

We have made use of identities such as

$$\exp(2\pi in)=1,\quad \exp(i\pi n_{d\uparrow})S_{d\uparrow\pm}=\mp S_{d\uparrow\pm},\ \text{etc.},$$

similar to those introduced in connection with the X-Y model.[4]

For the second transformation, we make use of the fact that the $S_{d\uparrow\pm}$ commute with $S_{d\downarrow\pm}$. Thus the 90° rotations can be performed independently:

II. $S_{d\downarrow z}\rightarrow S_{d\downarrow y}$ ($S_{d\downarrow x}$ invariant) and $S_{d\uparrow z}\rightarrow S_{d\uparrow x}$ ($S_{d\uparrow y}$ invariant).

In $\mathcal{H}$ this has an effect solely on the Coulomb term (I.2):

$$U(S_{d\uparrow z}S_{d\downarrow z})\rightarrow-\tfrac{1}{4}iU(S_{d\uparrow+}+S_{d\uparrow-})(S_{d\downarrow+}-S_{d\downarrow-}). \tag{II.1}$$

A final substitution inverts I, i.e., III (i) all $c_{k\downarrow}$, $c_{k\downarrow}{}^{*}$ stay the same; they are merely *relabeled* $b_{k\downarrow}$, $b_{k\downarrow}{}^{*}$ for notational consistency. (ii) Set

$$S_{d\downarrow-}\equiv b_{d\downarrow}\exp(i\pi\textstyle\sum n_{k\downarrow})\ \text{and}\ S_{d\downarrow+}\equiv\exp(i\pi\sum n_{k\downarrow})b_{d\downarrow}{}^{*}\quad(n_{k}\equiv b_{k\downarrow}{}^{*}b_{k\downarrow}).$$

(iii) Set

$$S_{d\uparrow-}\equiv b_{d\uparrow}\exp[i\pi(\textstyle\sum n_{k\downarrow}+n_{d\downarrow})]\ \text{and}\ S_{d\uparrow+}\equiv\exp[i\pi(\sum n_{k\downarrow}+n_{d\downarrow})]\,b_{d\uparrow}{}^{*}\quad(n_{d\downarrow}=b_{d\downarrow}{}^{*}b_{d\downarrow}).$$

(iv) Set

$$a_{k\uparrow}\equiv b_{k\uparrow}\exp[i\pi(\textstyle\sum n_{k\downarrow}+n_{d\downarrow}+n_{d\uparrow})]\ \text{and}\ a_{k\uparrow}{}^{*}\equiv\exp[i\pi(\sum n_{k\downarrow}+n_{d\downarrow}+n_{d\uparrow})]\,b_{k\uparrow}{}^{*}\quad(n_{d\uparrow}=b_{d\uparrow}{}^{*}b_{d\uparrow}).$$

The set of all b operators, together with their Hermitean conjugates, is a complete set of anticommuting field operators, related by a unitary transformation to the original set of c's. The Hamiltonian is quadratic in the new operators:

$$\sum\epsilon_{km}c_{km}{}^{*}c_{km}\rightarrow\sum\epsilon_{km}b_{km}{}^{*}b_{km}, \tag{III.1}$$

$$U(n_{d\uparrow}-\tfrac{1}{2})(n_{d\downarrow}-\tfrac{1}{2})\rightarrow\tfrac{1}{4}iU(b_{d\uparrow}{}^{*}+b_{d\uparrow})(b_{d\downarrow}{}^{*}+b_{d\downarrow}), \tag{III.2}$$

$$\sum_{km}V_{k}(c_{km}{}^{*}-c_{km})(c_{dm}{}^{*}+c_{dm})\rightarrow\sum V_{k}(b_{km}{}^{*}-b_{km})(b_{dm}{}^{*}+b_{dm}). \tag{III.3}$$

Quartic (or worse) terms would have resulted if $U\neq-2E_{d}$, or if a magnetic field acted on the d level. After transformation II, $\mathcal{H}$ would have contained terms linear in S_{dmx} or S_{dmy} which could not be handled exactly. Similar difficulties are found if $\mathcal{H}'$ is retained.

Nevertheless, we can study the effects of the transformation on any such nonlinear terms, and if they are of interest, treat their effect on $\mathcal{H}$ by perturbation theory.[5]

We now calculate the free energy F. In terms of the unperturbed, decoupled F_{0} at $\lambda=0$,

$$F(U,\lambda)=F_{0}(U)+\delta F, \tag{3}$$

where

$$\delta F=N^{-1/2}\textstyle\sum_{km}V_{k}\int_{0}^{\lambda}d\lambda\,\langle(b_{km}{}^{*}-b_{km})(b_{dm}{}^{*}+b_{dm})\rangle. \tag{4}$$

The thermodynamic averages indicated are readily obtained by means of Green functions.[6] Omitting the tedious but straightforward calculational details, we obtain an expression free of low-temperature anomalies,

$$\delta F=\int_{0}^{\lambda}d\lambda\int_{-\infty}^{\infty}d\omega f(\omega)(-i)[G(\omega-i\delta)-G(\omega+i\delta)], \tag{5}$$

where $f(\omega)$ is the Fermi function, and the Green function has the value

$$G(\omega)=\frac{(2\lambda/\pi)\{\omega[S_{\uparrow}(\omega)+S_{\downarrow}(\omega)]-8\lambda^2 S_{\uparrow}(\omega)S_{\downarrow}(\omega)\}}{[\omega-4\lambda^2 S_{\downarrow}(\omega)][\omega-4\lambda^2 S_{\uparrow}(\omega)]-\frac{1}{4}U^2}, \tag{6}$$

where

$$S_m(\omega)\equiv\frac{1}{N}\sum_k\frac{\omega V_k{}^2}{\omega^2-\epsilon_{km}{}^2}. \tag{7}$$

The transport properties are obtainable from the equations of motion:

$$\langle\langle c_{km}|c_{k'm}{}^*\rangle\rangle=\frac{\delta_{k,k'}}{2\pi}\frac{1}{\omega-\epsilon_k}+\frac{\lambda^2}{N}\frac{V_k}{\omega-\epsilon_k}G_{ddm}(\omega)\frac{V_{k'}}{\omega-\epsilon_{k'}}. \tag{8}$$

The transport lifetime is

$$\tau_{km}{}^{-1}\propto 2\,\mathrm{Im}G_{ddm}(\epsilon_k), \tag{9}$$

where

$$G_{ddm}(\omega)=\langle\langle c_{dm}{}^*+c_{dm}|c_{dm}{}^*+c_{dm}\rangle\rangle. \tag{10}$$

An evaluation of these transport properties (in which we *do* find a low-T "Kondo effect") will be given elsewhere.[5]

We conclude the present work by a comparison of the free energies F of $\mathcal{H}$ and F_A and $\mathcal{H}_A$. As we may use the eigenstates of our model for a variational evaluation of $\mathcal{H}_A$, we can obtain $F(\lambda)>F_A(2\lambda)$. On the other hand, $F(2\lambda)<F_A(2\lambda)$. Combining these,

$$F(\lambda)<F_A(\lambda)<F(\tfrac{1}{2}\lambda). \tag{11}$$

In the limit $T=0$ we see that these inequalities also hold for the respective ground-state energies. As the upper and lower bounds differ by $O(\lambda^2)$, F_A becomes adequately circumscribed in the weak-coupling limit ($\lambda^2\to 0$).

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[1]P. W. Anderson, Phys. Rev. 124, 41 (1961).

[2]See reviews by A. Heeger, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23; J. Kondo *ibid.*

[3]More recent approaches, based on sophisticated funtional integration methods, may be found in S. Wang, W. Evenson, and J. R. Schrieffer, Phys. Rev. Lett. 23, 92 (1969); D. Hamann, *ibid.* 23, 95 (1969); D. Amit and C. Bender, to be published.

[4]See the discussion in E. Lieb and D. Mattis, *Mathematical Physics in One Dimension* (Academic, New York, 1966).

[5]I am presently studying the paramagnetic susceptibility by this method, as well as the interaction between two impurities and the transport properties of my model (to be published).

[6]D. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys. Usp. 3, 320 (1960)].

Ground-State Energy of an Exciton-Donor Complex Calculated in a "Two-Polaron Model"*

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The ground-state energy of an exciton bound to ionized donors in III-V and II-VI compounds is calculated with the electron-phonon coupling taken into account. Results for thirteen crystals are in very good agreement with the available experimental data.

Though exciton theory has considerably improved the understanding of the luminescence spectra in the band-edge region, a further extended theory had to be developed for the interpretation of certain lines beneath free exciton lines. Led by a proposal of Lampert,[1] bound excitons have thus been intensively investigated during the last years, as reviewed by Thomas,[2] Johnson,[3] Halsted,[4] and Reynolds, Litton, and Collins.[5] As in the case of a free exciton, however, the electron-phonon coupling has to be taken into account for a precise calculation of